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# Technological Advances in Refining and Processing of Stainless Steel—a Brief Overview

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**Abstract.** The world production of stainless steels (SS) has witnessed considerable growth over the last 15 years with a continuing rise in the demand. The production level has soared from 12 million tons per annum to more than 25 million tons per annum at present. Although stainless steel is more expensive than conventional steels such as mild, HSLA and high carbon grades, its cost is far outweighed by its benefits. Perceived continued growth in the demand, and favourable investment returns have encouraged the modifications, innovations and expansion of existing facilities. This chapter addresses some aspects of recent advances in the area of refining, process innovations and developments in stainless steel production. These include a brief account of phase equilibria for stainless steel, specialized refining technologies such as argon oxygen decarburization (AOD), vacuum oxygen decarburization (VOD), AOD-VCR and electroslag refining (ESR). Some typical issues of quantitative modelling and simulation methodologies applied to stainless steel refining processes as an innovative tool for enhancement of process understanding and control have also been discussed.

**Keywords:** *Stainless steel, secondary steel making, phase equilibria, steel refining, process innovation, process modelling*

## 29.1 Introduction

The world production of stainless steels has witnessed considerable growth over the last 15 years and continues to rise. From about 12 million tons/annum the present level exceeds 25 million tons/annum. Although this steel is more expensive than conventional steels such as mild, HSLA and high carbon grades, its cost is far outweighed by its benefits. Demands of stainless steel worldwide appear to be growing at an average rate of 5% to 7%. Perceived continued growth in demand and favourable investment returns has encouraged the modifications, innovations and expansion of existing facilities.

'Stainless' is a term coined early in the development of these steels, for cutlery products. It has since been adopted as a generic name and, now, covers a wide range of steel types and grades for corrosion or oxidation resistant applications. The minimum chromium content of standard stainless steels is 10.5%.<sup>1</sup> Other alloying elements, particularly nickel, molybdenum and nitrogen, are added to modify their structure and enhance properties such as formability, strength and cryogenic toughness. Stainless steels owe their corrosion resistance to the presence of a 'passive', chromium-rich, oxide film that forms naturally on the surface. However, stainless steels are not 'indestructible'.

Stainless steels are commonly divided into five groups:

- Martensitic stainless steels
- Ferritic stainless steels
- Austenitic stainless steels
- Duplex (ferritic-austenitic) stainless steels
- Precipitation hardening stainless steels.

*Martensitic stainless steels* are essentially alloys of chromium and carbon that possess a martensitic crystal structure in the hardened condition. They are ferromagnetic, hardenable by heat treatments, and are usually less resistant to corrosion than some other grades of stainless steel. The chromium content usually does not exceed 18%, while the carbon content may exceed 1.0%. The chromium and carbon contents are adjusted to ensure a martensitic structure after hardening. Excess carbides may be present to enhance wear resistance or as in the case of knife blades, to maintain cutting edges.

*Ferritic stainless steels* are chromium containing alloys with ferritic, body centered cubic (bcc) crystal structures. Chromium content is typically less than 30%. The ferritic stainless steels are ferromagnetic. They may have good ductility and formability, but high temperature mechanical properties are relatively inferior to the austenitic stainless steels. Toughness is limited at low temperatures and in heavy sections.

*Austenitic stainless steels* have a austenitic, face centered cubic (fcc) crystal structure. Austenite is formed through the generous use of austenitizing elements such as nickel, manganese and nitrogen. Austenitic stainless steels are effectively nonmagnetic in the annealed condition and can be hardened only by cold working. Some ferromagnetism may be noticed due to cold working or welding. They typically have reasonable cryogenic and high temperature strength properties. The chromium content is typically in the range of 16% to 26%; the nickel content is generally less than 35%.

*Duplex stainless steels* are a mixture of bcc ferrite and fcc austenite crystal structures. The percentage of each phase is dependent on the composition and heat treatment. Most duplex stainless steels are intended to contain around equal amounts of ferrite and austenite phases in the annealed condition. The primary alloying elements are chromium and nickel. Duplex stainless steels generally have similar corrosion resistance to austenitic alloys except that they typically have better stress corrosion cracking resistance. Duplex stainless steels also generally have greater tensile and yield strengths, but poorer toughness than austenitic stainless steels.

*Precipitation hardening stainless steels* are chromium-nickel alloys. Precipitation hardening stainless steels may be either austenitic or martensitic in the annealed condition. In most cases, precipitation hardening stainless steels attain high strength by precipitation hardening of the martensitic structure.

Stainless steel was discovered independently, around 1913, by researchers in Britain and Germany. The first true stainless steel was melted on the 13th August 1913, in Sheffield, on the initiative of Harry Brearley. This steel was martensitic with 0.24% carbon and 12.8% chromium. The first duplex stainless steels were produced in Sweden, around 1930, for applications in the paper industry. New grades with a better weight-to-strength ratio were then required for jet aircrafts, which led to the development of the precipitation hardening grades such as 17:4 PH.<sup>1,2</sup> The basic metallurgy of the iron/chromium and iron/chromium/nickel systems was understood by about 1940, and by the 1950s, stainless steels were standardized in specifications that have changed little since then. As these standard grades were accepted, the emphasis changed to finding cheaper mass production methods, and popularizing the use of stainless steel.

Prior to the late 1940s, stainless steel was made in the electric arc furnace by melting carbon steel scrap, iron ore, burnt lime and adding low carbon ferrochrome to attain the specified chromium. In this process (known as the 'rustless process'), most stainless grades were made to target carbon specification of 0.08%. During this period, the only practical and economic way to use stainless steel scrap was to remelt it in induction furnaces. With the introduction of tonnage oxygen in the steel industry in the late 1940s, a new arc furnace practice evolved in which stainless steel scrap, high carbon ferrochrome, nickel, and lime were melted. The bath was blown with oxygen to temperatures between 1850 and 1950°C, reduced with silicon and aluminum, and trimmed with low carbon ferrochrome. Relative to the rustless process, this practice resulted in significant reduction in power consumption, process time and the use of expensive low carbon ferrochrome as well as improved quality of steel (decreased hydrogen contents) and increased chromium recoveries.

In 1954, W Krivsky of Union Carbide<sup>2</sup> was studying carbon-chrome-temperature relationships in ferrochromium melting in the laboratory. The experiments involved blowing oxygen onto the surface of molten chromium alloy baths under isothermal conditions. In order to control temperature, argon has been added to decarburize the melt to low carbon levels without excessive chromium oxidation. Krivsky's observation led to plant-scale experiments injecting argon/oxygen mixtures by lance into the arc furnace between 1958 and 1962. Eventually, it was concluded that a separate refilling vessel (duplex process) was necessary to develop a commercial process. The next leap in stainless steel development was

made possible by the development of the argon oxygen decarburization (AOD) process, in the late 1960s. This technique made it possible to produce much cleaner steels with a very low carbon level and well-controlled nitrogen content.

The introduction of continuous casting in stainless steel production, in the 1970s, has contributed to lower production costs and higher quality. Since then, the addition of nitrogen and lowering of carbon content has made it possible to develop the duplex stainless steels into readily weldable materials. The last two decades have seen the introduction of the 'super' stainless steels. Superferritic grades with very low interstitial levels and high chromium and molybdenum contents have superior corrosion resistance compared to standard ferritic grades. However, although these steels have found certain applications, their success has been limited. The highly alloyed superaustenitic and superduplex stainless steels, with excellent corrosion resistance and better fabricability and weldability than the ferritic steels, have found a more widespread use and are today important engineering alloys. Supermartensitic steel is the most recent contribution to the stainless family.<sup>3,4</sup> These steels are extremely low in carbon (typically  $<0.010\%$ ) and offer a combination of high strength, adequate corrosion resistance and weldability at a competitive price. Figure 29.1 shows the generic process chain for the manufacturing of steel including stainless steel.

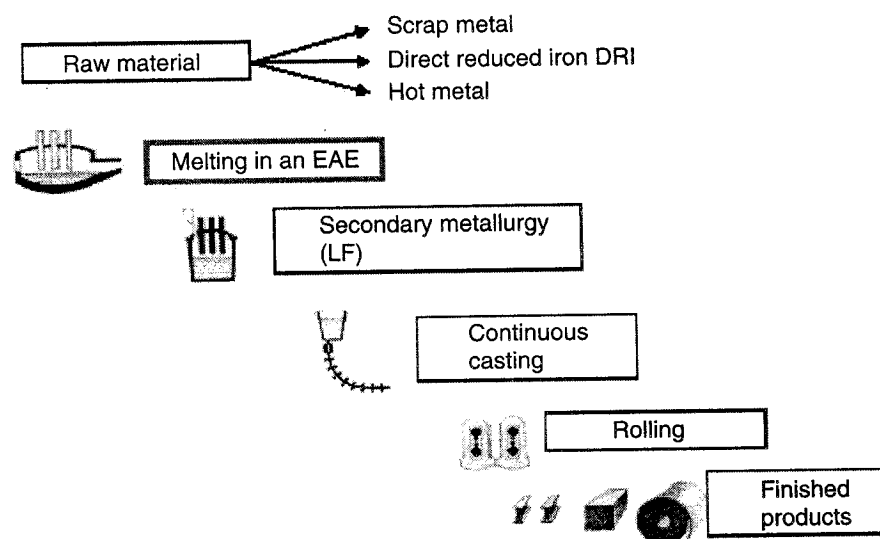


Fig. 29.1 Steel making process chain for stainless production.

During various process innovation studies, mathematical and physical modelling have been utilized as the standard tools in characterizing and quantifying process variables which facilitate new process development, optimization and control. Further mathematical models are being applied to quantify and investigate interactions between various phenomena in stainless steel making operations which primarily encompass thermochemistry, phase transformation, refining, continuous casting operations and a host of other pertinent areas.



In this chapter, some of the issues pertaining to phase equilibria, advancement in refining operations at industrial scale and modelling of stainless steel production processes have been discussed.

## 29.2 Phase Equilibria of Stainless Steel

Most of the stainless steels are based on the Fe–Cr–C and Fe–Cr–Ni–C systems,<sup>5,6</sup> but other alloying elements are also important. Iron and its alloys can exist in several crystallographic forms, of which the most common are the body centred cubic (bcc) and face centred cubic (fcc). In pure iron, the fcc structure persists between 910 and 1400°C, the bcc structure below and above this interval (up to the melting temperature of 1539°C). This transformation allows a wide range of microstructures to be achieved by controlled heat treatment. Mechanical properties such as strength and toughness are essentially related to the microstructure, and can therefore be obtained in an extraordinarily large range of strength or toughness. Stainless steels are routinely produced with strengths from 100 MPa to more than 1 GPa.

Knowledge of the relative stabilities of the bcc and fcc structures of iron alloys is therefore of prime concern. For this reason, and also because Cr and Ni are the most important alloying elements in stainless steels and form the reference relative to which the influence of other solutes is classified.<sup>7,8</sup> These have long been used as reference to quantify the influence of alloying elements on the bcc  $\longleftrightarrow$  fcc phase transition. The elements like Cr, which promote ferrite, are called *ferrite stabilizers* and those like Ni which promote austenite are called *austenite stabilizers*. The equations below give a rough guide of the potency of individual elements to act as ferrite or austenite stabilizers when compared to the corresponding effects of Cr and Ni respectively (concentrations in wt%):

$$\text{Cr equivalent} = \text{Cr} + 2\text{Si} + 1.5\text{Mo} + 5\text{V} + 5.5\text{Al} + 1.75\text{Nb} + 1.5\text{Ti} + 0.75\text{W}$$

$$\text{Ni equivalent} = \text{Ni} + \text{Co} + 0.5\text{Mn} + 0.3\text{Cu} + 25\text{N} + 30\text{C}$$

Without carbon, the limit beyond which austenite no longer forms is about 13.5 wt% chromium. However, additions of carbon help stabilize the austenite and therefore increase this limit (Fig. 29.2).

Chromium and nickel equivalents<sup>6,8,9</sup> are also used in the welding industry to evaluate the microstructures obtained when a weld solidifies and cools to ambient temperature (Fig. 29.3). Although these diagrams are popular, it should be understood that they are not phase diagrams but rather represent the microstructures obtained under specific cooling conditions.

### 29.2.1 Precipitate phases

These include carbides, nitrides or intermetallic compounds. Since most stainless steels serve at ambient temperature, the intermetallic compounds are of little relevance as they are extremely slow to precipitate because even though they may be thermodynamically stable phases, they are difficult to nucleate. It is evident from Fig. 29. 2 (Fe–Cr–C phase diagram)

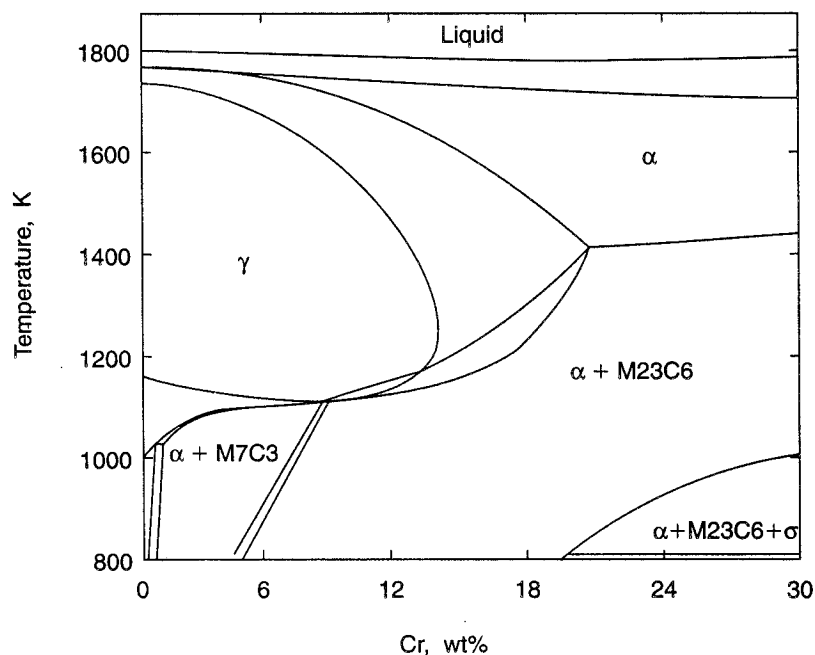


Fig. 29.2 Vertical section of Fe-Cr-C diagram for 0.1C wt%.<sup>6</sup>

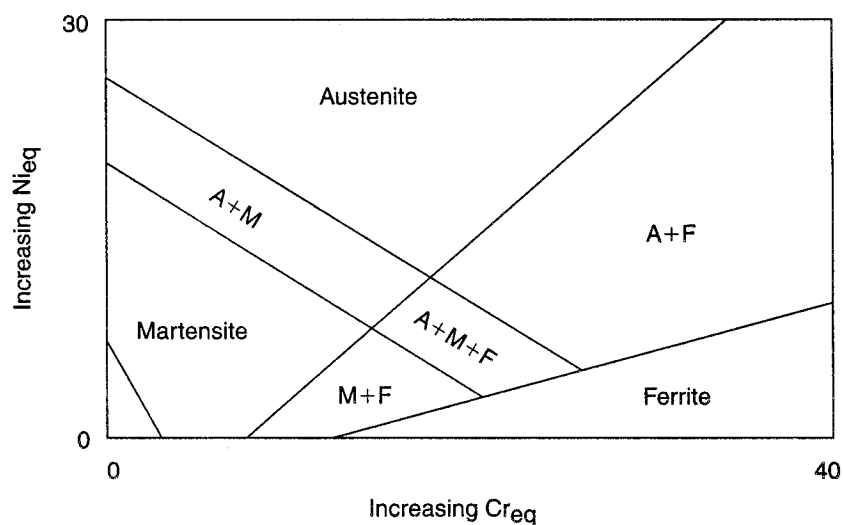


Fig. 29.3 Schaeffler diagram for weld metals.<sup>6</sup>

that typical martensitic steels should exhibit ferrite and  $\text{M}_{23}\text{C}_6$  in equilibrium at for example, 600°C. In practice, this carbide is only found after relatively long ageing, because it is preceded by intermediate phases in the sequence cementite,  $\text{M}_2\text{X}$  and  $\text{M}_7\text{C}_3$ , leading finally to  $\text{M}_{23}\text{C}_6$ .

These precipitation sequences become more complex in heavily alloyed ferritic or austenitic stainless steels, such as those designed for the power generation industry. Considerable effort is

being devoted to understanding and estimating the precipitation sequences in such alloys because these are intended to serve safely for 30 or more years, that is for time periods far in excess of what can be reasonably achieved in the alloy development exercise.<sup>6,7,9</sup> Figure 29.4 shows the phase diagram for stainless steel at 900°C.

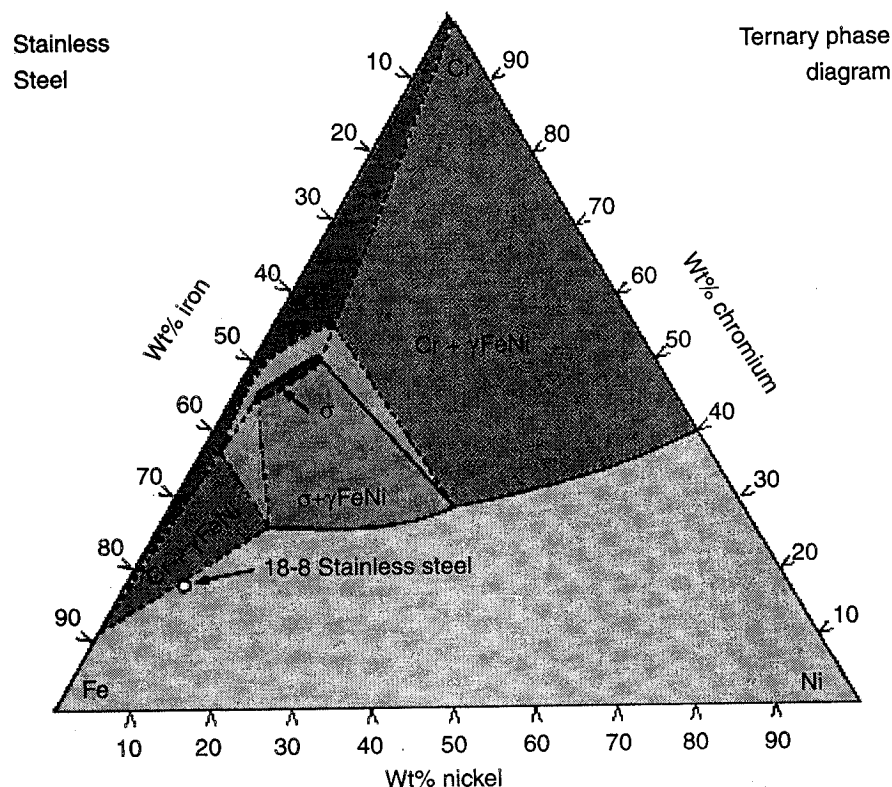


Fig. 29. 4 Stainless steel phase diagram at a temperature of 900°C.

### 29.2.2 Martensite formation

Most stainless steels have a high hardenability, meaning that the reconstructive transformation of austenite to (ferrite + carbides) is unlikely to happen unless the steel is cooled slowly. The most important features of these martensitic alloys are therefore the martensite start ( $M_s$ ) and finish temperatures ( $M_f$ ). For martensitic steels, the range  $[M_s - M_f]$  should be above the room temperature to ensure fully martensitic structure. On the contrary, the  $[M_s - M_f]$  range of austenitic stainless steels is often well below 0°C, which is why they can be used in cryogenic applications; austenite does not have the classical ductile–brittle transition associated with body centred cubic iron (martensite, ferrite). Cold deformation can induce martensitic transformation to  $\alpha$  and  $\epsilon$  martensite, the extent depending on the strain and on the chemical composition. Heavily alloyed austenitic steels with up to 20Cr and 25Ni wt% are fully stable.

On the basis of their main microstructural features, there exist the following key categories of stainless steels:

- *Martensitic stainless steels*, typified by types 410/420/440, containing about 12Cr and 0.1C wt% as the basic composition, leading to a fully martensitic microstructure at room temperature.
- *Ferritic stainless steels* containing larger amounts of Cr which stabilises the ferritic phase.
- *Austenitic stainless steels*, such as type 304 typically contain 18Cr and 8Ni wt%; the nickel balances the effect of chromium stabilise the austenitic phase; the nickel also makes the alloy more expensive than the martensitic variants. The large substitutional content depresses the  $M_s$  temperatures well below 0°C.
- *Duplex stainless steels*, whose microstructure is approximately made up of 50/50 ferrite/austenite and in many applications are less expensive and stronger than the fully austenitic variants.

### 29.3 Advances in Stainless Steel Refining Technology

Over the past couple of decades, major changes have taken place in stainless steel making practice. Stainless steel production also encompasses traditional steel making practices involving the direct transfer of liquid steel via a ladle from the basic oxygen steel making (BOS) vessel or electric arc furnace (EAF) to the casting bay where the steel was cast into ingots. Only crude composition and temperature control were possible by this route.

In the 1950s, the first attempts were made to remove hydrogen by vacuum degassing. More recently, vacuum degassers have been used to produce ultra-low carbon (ULC) steels with carbon contents less than 30 ppm (0.003 wt). The CAS-OB process (composition adjustment by sealed argon bubbling with oxygen blowing) provides a convenient way of making alloy additions in an inert environment, thereby improving the steel cleanliness and the 'recovery rate' of the added components. The recovery rate is the amount of the added element that actually increases the steel composition rather than being lost to the slag or atmosphere. Since many secondary steel making processes result in significant changes in temperature, it is very often necessary to reheat the ladle steel between processes and/or before casting. Two methods are commonly used: electrical reheating via a ladle arc furnace, and chemical reheating by the injection of oxygen and aluminum (or silicon), which react exothermically to generate heat.

Stainless steel is also produced in the EAF, recycled steel scrap is melted and converted into high quality steel (including stainless steel) by using high power electric arcs. The main task of most modern EAFs is to convert the solid raw materials to liquid crude steel as fast as possible and then refine further in subsequent secondary steel making processes. Nevertheless, if time is available, almost any metallurgical operation may be performed during flat bath operation period (after melting), which is usually performed as a pretreatment to the secondary steel making operations.

All secondary steel making processes as applicable to production of stainless steel share similar characteristics including: theoretical concepts, raw material savings, productivity

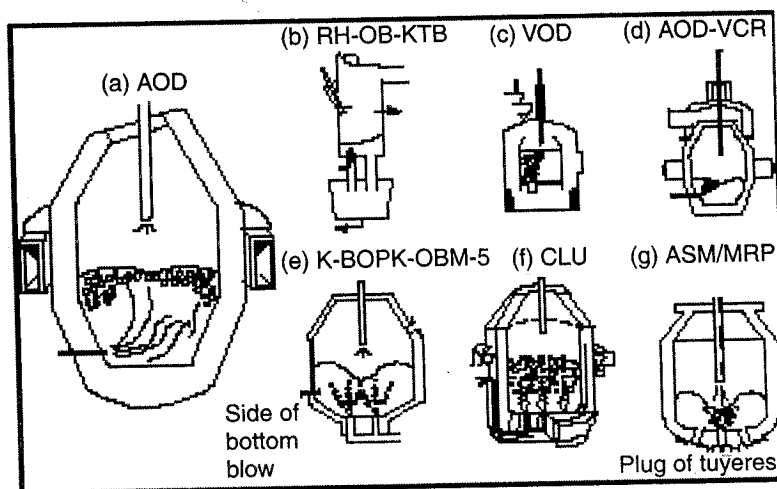


Fig. 29.5 Secondary steel making processes for stainless steel production.

increase and quality improvements, specialized equipment and vessel operation. During the late 1950s, vacuum degassing processes (for example, DR, RH, ASEA-SKF, Finkl VAD) were developed for carbon steel production, and led to the development of vacuum decarburization processes for stainless steels in the mid-1960s.<sup>5</sup> The VOD (vacuum oxygen decarburization) process was developed by Witten (now Thyssen) in Germany between 1962 and 1967. Between 1959 and 1962 stainless steel has been produced in a LD converter by Witten (decarburization of pig iron, addition of low carbon ferrochrome, and reduction with silicon and aluminum). With the installation of ladle vacuum degassing unit in 1962, trials were conducted duplexing pre-melt from the LD to the vacuum degasser. Initially, iron ore was used for decarburization. Later, pre-melting took place in the arc furnace, and oxygen was top blown onto the bath surface in the degassing ladle. Figure 29.5 is a schematic that illustrates the various types of secondary steel making processes used to produce stainless steels. The AVR process, in which oxygen is injected below the surface by top lance in the degassing ladle, was developed by Allegheny Ludlum in the mid-1960s. The development of the AOD and VOD processes between 1954 and 1968 revolutionised stainless steel making and was the primary impetus for the dramatic growth in production between 1970 and the present. The use of these processes resulted in significant reduction in raw material costs, enhancement in productivity and improvement in quality. Figure 29.6 shows the percentage contribution of various refining processes in the production of stainless steel. It may be observed from the figure<sup>5,10,11</sup> that the predominant route for the production of stainless steel is through AOD process.

### 29.3.1 Argon oxygen decarburization (AOD)

The bulk of the stainless production in 1996 in this category was made in the CLU at Columbus in South Africa (280,000 tons), at the Degefors plant of Avesta Sheffield in Sweden (180,000 tons), in the ASM at Jindal in India (90,000 tons), and in NKK's SFR in Japan (90,000 tons).

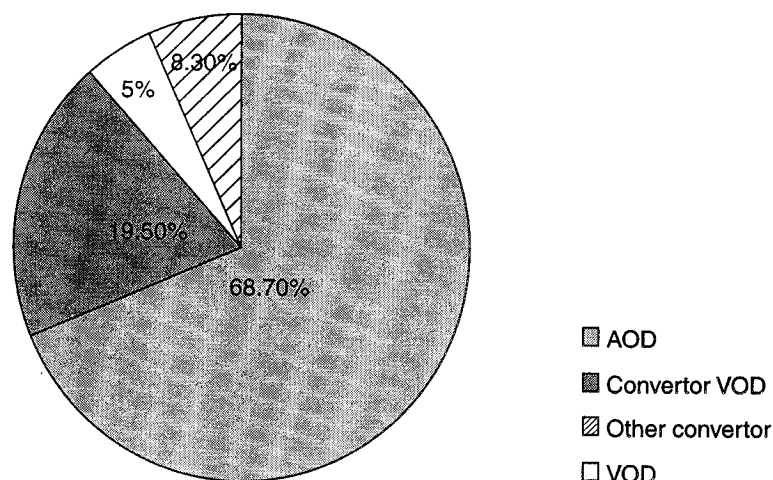


Fig. 29.6 Stainless steel production through various routes (in percentage).

Presently, there are over 60 AOD steel mill installations worldwide producing about 69% of the total stainless steel in western world. There are a similar number of AOD foundry installations.

The rapid acceptance of the AOD process by a majority of worldwide stainless producers is indicative of its capability to economically produce a high quality product from least cost charge materials. Continued new developments in AOD practices and equipment have kept the process competitive with respect to operating costs and productivity relative to other processes. These include: the development of optimum techniques for top blowing; reliable process control models to predict carbon and temperature endpoints; brick thickness zoning increases in the tuyere pad area; and practices to optimize economic production of ultra-low carbon and nitrogen low-chrome ferritic grades of stainless steel.

With respect to the latter development, all of the producers of ultra-low carbon and nitrogen ferritic grades (409L and 439L) listed are AOD producers. Carbon and nitrogen levels similar to those obtained on 16% to 18% chromium ferritic grades are also obtained on austenitic grades of similar chromium content.

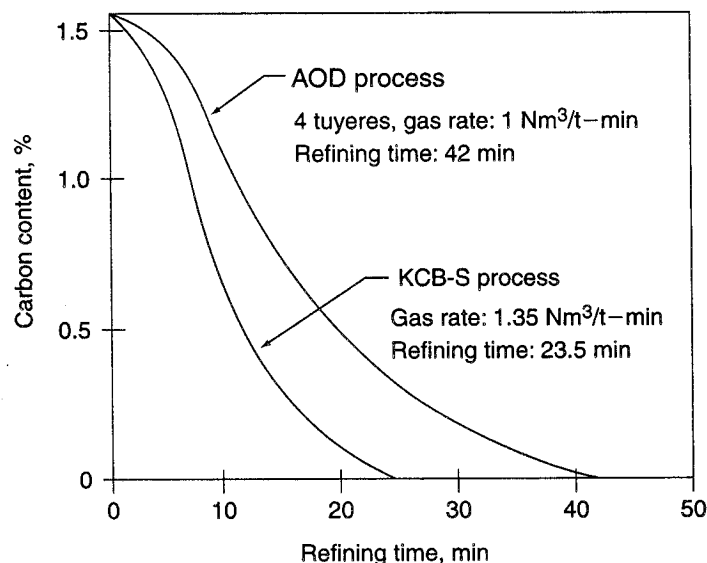
The use of irregular shaped tuyeres evolved from laboratory and 90-ton plant scale trials have been made at Sumitomo in the early 1980s. These trials indicated significant improvement in refractory life and reduced inert gas stirring requirements using tuyere shapes which minimize jet collapse (back attack). Engineering problems associated with the manufacture of such a tuyere and tuyere brick, as well as the question of how to assure equal distribution of shroud gas over the perimeter of the tuyere, have hindered widespread adoption of this idea.

The CLU converter process was developed by Uddeholm in Sweden and Creusot Loire in France. The first commercial installation was made at Degefors in Sweden (now part of Avesta Sheffield) in 1973. The process is bottom blown and originally, steam was used

as a diluent throughout the decarburization steps, and argon consumption was, reduced by about 80% relative to the AOD process. However, the silicon consumption increased by 250% due to increased metallic oxidation below 0.18% carbon. The process has evolved to use various amounts of nitrogen, argon and steam depending on nitrogen and hydrogen aims. The process is used by Samancor in the production of medium carbon ferrochrome in South Africa and Maharashtra in India. One of the recent installations (1995) is the 100-ton converter at Columbus in South Africa. The justification for the Columbus installation is based on their lack of cooling material. The lack of argon availability and/or high argon price are other reasons to justify the CLU process. While argon consumption is lower, silicon and refractory consumptions are higher, and maintenance requirements (associated with steam generation) are greater than in other converter processes.

The K-OBM-S process<sup>5,12</sup> evolved from Kawasaki's K-BOP process (described in the 'ConverterNacUln Processes' section) which, in turn, evolved from the OBM practice as formerly used on stainless steel. K-OBM-S is similar to the modem AOD (top blown with a lance and either bottom or side blown with tuyeres). Its features include: high blow rates, the addition of energy sources such as carbon, the use of hydrocarbon shroud gases, post combustion, and lime powder injection (all of which may be included in the modem AOD depending on the steelmakers' needs and the degree of flexibility desired). The KOBM-S is promoted as a bottom blown process; however, two of the first four installations (POSCO in Korea and Bolzano in Italy) are side blown. In these installations, the K-OBM-S is used to finish the bulk of the production, which is then transferred directly to the ladle treatment station and/or continuous caster. In the other two installations, ISCOR and Microsteel in South America, the converter is bottom blown to intermediate carbon content and then transferred to a VOD (triplex process). All four of these installations were started up in 1996. Proponents of side blowing claim that higher carbon removal efficiencies are obtained in the range of 0.1% to 0.005% carbon (due to longer inert gas bubble residence time), and improved desulphurization is obtained in the range of 0.005 to less than 0.001% sulphur (due to improved mixing). The MRP and ASM processes, developed by the major German steel mill equipment suppliers (MDH and MAN GHH), are similar to the AOD process except that they are bottom blown (with or without a top lance). In some installations, the MRP process is operated using alternate periods of oxygen and inert blowing rather than mixtures (the concept is similar to argon decarburisation in the AOD). The use of MRP or ASM without VOD is essentially limited to companies in India and several small installations in Germany. To the extent that these vessels are operated as an AOD, operating costs are similar to that of AQDs regular carbon grades.

In converter processes, the vessel is usually charged with de-slagged metal and blown at oxygen/inert ratios of 3/1 to 5/1 through the tuyeres and 100% oxygen through the top lance. The adaptation of the top lance to bottom or side blown converters has significantly reduced converter processing costs and increased productivity. An example of the effect of top blowing with a 'hard blow' (essentially 100% oxygen reacting with the bath) on decarburization time relative to operation without a top lance in a side blown converter is shown in Fig. 29.7.



**Fig. 29.7** Decarburization comparison of an AOD without the top lance versus an AOD with the hard blow top lance.<sup>5</sup>

Table 29.1 summarizes<sup>5</sup> typical and best results currently obtained in operating AOD vessels. It should be recognized that there are inherent difficulties in making generalizations applicable to AOD operators worldwide since there are wide variations in raw materials, product mixes, equipment, practices and economic conditions. Further, some of the improvements used by the majority of AOD operators have not been universally adopted.

Simultaneously, many studies on mathematical modelling for the AOD refining of stainless steel have been carried out, and numerous models have been proposed and developed to attempt to accomplish optimisation and computer control of the process.

### 29.3.2 Vacuum oxygen decarburization processes (VOD)

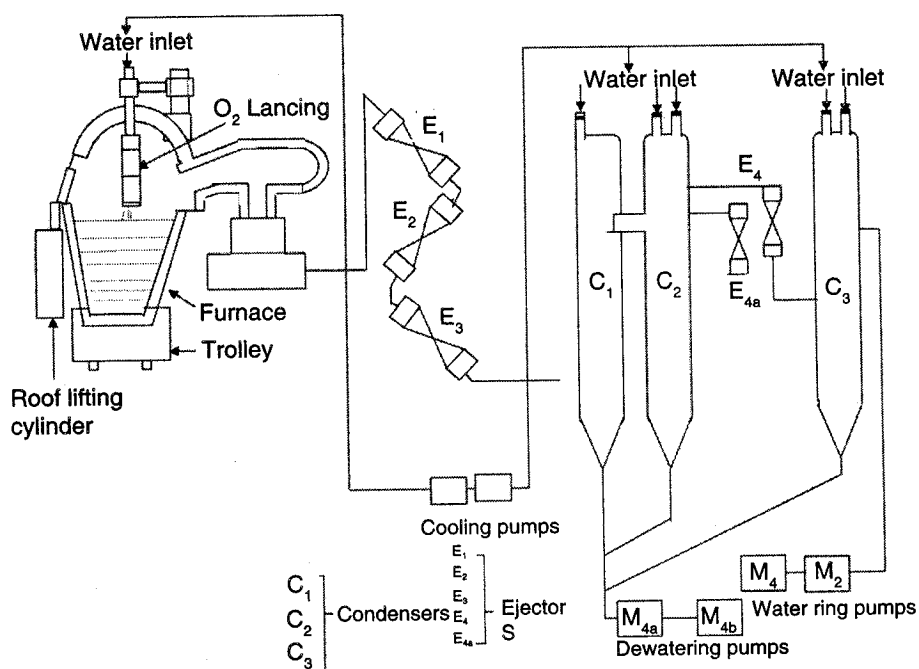
VOD and other vacuum processes (fed directly from the EF or LD) account for about 6.8% of the overall production. The bulk of this production is made in Japan (about 400,000 tons) with significant amounts being made in China and Canada, and to a lesser extent in the United States, the United Kingdom, Germany, France, and India. Most vacuum production (probably 98%) is made using the VOD process. As previously noted, the process was developed at Witten (Thyssen) in Germany between 1962 and 1967. Its major attributes include a minimal consumption of argon (for example, about 1 cubic meter/ton of steel), and the elimination of nitrogen pick-up during tap associated with converter processes (since the VOD ladle is the casting ladle). Silicon consumption in the VOD is only 3 kg/ton; however, because of the 0.3% carbon and less than 0.1% silicon VOD charge requirement, an additional 3 kg/ton of silicon is used to minimize chromium losses in the arc furnace. Figure 29.8 depicts the schematic of VOD process.



**Table 29.1** AOD consumption when producing AISI 304 in an 80-ton vessel\*

	Typical	Best
Argon, Nm <sup>3</sup> /ton	12	9
Nitrogen, Nm <sup>3</sup> /ton	9–11	9
Oxygen, Nm <sup>3</sup> /ton	25–32	—
Lime, kg/ton	50–60	42
Spar, kg/ton	3	2
Aluminum, kg/ton	2	1
Silicon (reduction), kg/ton	8–9	6
Brick, kg/ton	5–9	2
Decarbmetallics, kg/ton	135	—
Charge to tap time, min	50–80	40
Total Cr yield, % EAF/AOD	96–97	99.5
Total Mn yield, % EAF/AOD	88	95
Total metallic yield, % EAF/AOD	95	97

\* 1.8 start carbon, 0.05% Nz, 0.005% S

**Fig. 29.8** Schematic of VOD process.

In the early 1970s, Kawasaki Steel developed SS-VOD, which included modifications to the standard VOD such as multiple porous plugs and argon O-ring sealing. This process is now used primarily for making extra-low carbon and nitrogen ferritic grades having chrome contents between 22% and 30% to reach maximum carbon and nitrogen levels of 30 and 60 ppm, respectively. Maximum carbon and nitrogen levels reached on percentage chromium grades were 15 and 30 ppm, respectively.

However, the typical treatment time is 120 to 180 minutes. By way of comparison on 18% chrome grades, standard VODs obtain maximum carbon and nitrogen levels of 60 and 90 ppm, respectively. Recently in Japan, the PB process (powder blowing through top lance onto the bath under vacuum) has been adopted by VOD operators to improve desulphurization. In both applications, the time of the VOD process is decreased. Up until mid-1995, a significant amount of stainless steel was being produced in the KTB or modified RH-OB process at Kawasaki Chiba. In this process, after the decarburization using the K-BOP converter to about 0.12% carbon, steel was transferred to the KTB for final decarburization and finishing.

### 29.3.3 AOD-VCR process

This process, developed at Daido Shibukawa in 1989, combines AOD and VOD in the same converter. It is used at Daido Chita and was adapted to the AOD at Nippon Steel. Predecessors to this process were the Dgine vacuum converter process developed in the mid-1970s and the VODC or VODK process developed at Witten between 1973 and 1976. The VODC is typically blown with a top oxygen lance and with a single tuyere in the vessel bottom.

The AOD-VCR operates as a conventional AOD down to a carbon level of 0.08%–0.10%. The process is stopped for sampling and a vacuum lid is put into place (sealed to a flange located about halfway up the conical section of the converter). A vacuum is pulled and used for the remainder of decarburization and reduction (desulphurization is carried out in the transfer ladle prior to AOD charge). The major advantage of this process relative to the converter processes is the decreased argon and silicon consumptions. The disadvantages include: higher refractory consumption, a reduced ability to melt scrap, maintenance and costs associated with steam production. The actual time of operation (including turndown for sampling, exchanging hoods, lip seal maintenance, pulling and breaking vacuum) is longer than that for a modem AOD on regular carbon grades. Relative to having separate converter and VOD units, the AOD / VCR has higher operating costs (silicon, refractory, and argon), lower productivity and higher nitrogen contents. However, capital costs may be somewhat lower.

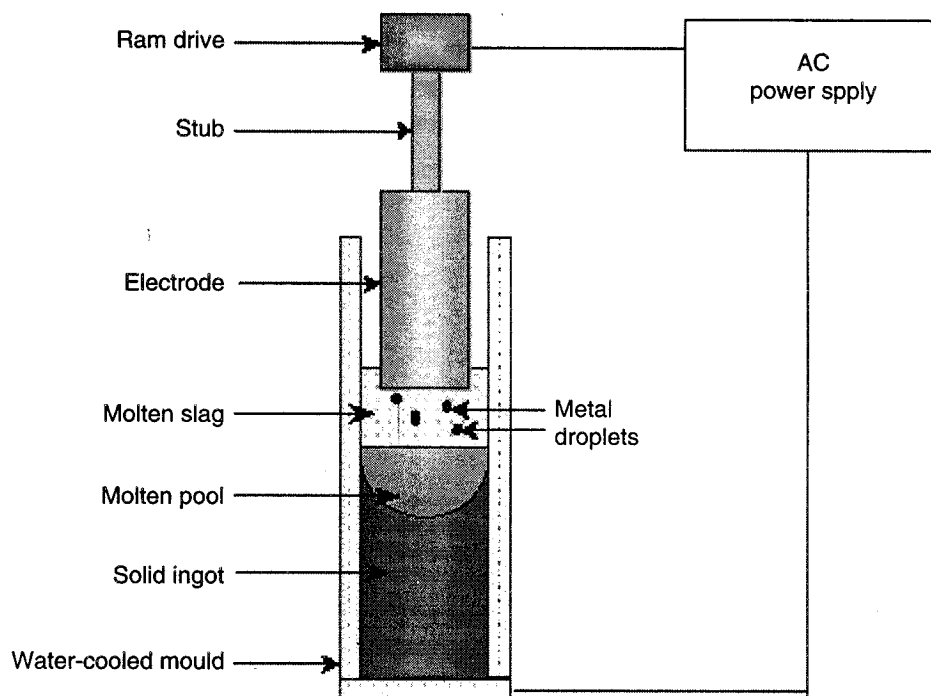
### 29.3.4 Electroslag refining (ESR) process

ESR has been known since the 1930s, but it took approximately 30 years before it became an acknowledged process for mass production of high-quality ingots including stainless steel. The ESR technology is of interest not only for the production of smaller weight ingots of tool steels and superalloys, but also of heavy forging ingots up to raw ingot weights of 165 tons.

Whereas VAR needs vacuum for refining, in ESR the consumable electrode is dipped into a pool of slag in a water cooled mould. An electric current (usually AC) passes through

the slag, between the electrode and the ingot being formed and superheats the slag so that drops of metal are melted from the electrode. They travel through the slag to the bottom of the water-cooled mould where they solidify. The slag pool is carried upwards as the ingot forms. The new ingot of refined material builds up slowly from the bottom of the mould. It is homogeneous, directionally solidified and free from the central unsoundness that can occur in conventionally cast ingots as they solidify from the outside inwards.

Generally the ESR process offers very high, consistent and predictable product quality. Finely controlled solidification improves soundness and structural integrity. Ingot surface quality is improved by the formation of a solidified thin slag skin between ingot and mould wall during the remelting operation. This is why ESR is recognized as the preferred production method for high-performance superalloys and strategic grade steels that are used today in industries such as aerospace and nuclear engineering as well as for heavy forgings. Ingots are obtained with purity levels that were unheard of some years ago. Other branches of engineering are following the examples of the 'high-tech' pacesetters and insist on new, high purity levels that can be obtained from ESR with the latest, most sophisticated equipment. Figure 29.9 shows the schematic of ESR process.



**Fig. 29.9** Schematic of the ESR process.

The slag in the ESR process for the production of high quality alloys is crucial for its success.<sup>12</sup> The ESR slag composition for the stainless steel refining operation is approximately 60%  $\text{CaF}_2$ –20%  $\text{CaO}$ –20%  $\text{Al}_2\text{O}_3$  by weight.

The slag must have a low partition ratio for the contaminants between the metal and the slag. It allows most of the contaminant to be incorporated in the slag phase. Its interfacial

properties must be such that it wets the metal for effective removal of the contaminants, but it must not facilitate formation of slag skin around the ingot. It is desirable to minimize the slag skin around the ingot. The electrical conductivity must be such that it provides efficient joule heating. A high melt rate of the electrode results in a high production rate, however this condition does not necessarily optimize the end product (recycled stainless steel) in the ESR process.<sup>13</sup> Conversely, a very low melt rate in the ESR process causes the solidified ingot to have coarse crystalline grains and poor surface finish. Hence, an accurate knowledge of the ESR slag conductivity is necessary for establishing a control strategy for obtaining the desired melt rate in the ESR process. Thus, the electrical conductivity of the slag may be used as one of the input parameters in the ESR process control model.

#### *Pressure electroslag remelting (PESR)*

Over the past 30 years, nitrogen has become increasingly attractive as an inexpensive alloying element for enhancing certain properties of steel. In austenitic grades of steel including stainless steels, nitrogen, particularly in the dissolved form, increases yield strength by forming a super-saturated solid solution. With ferritic steel grades, the aim is to achieve a fine dispersion of nitrides comparable to the microstructure obtained by quenching and tempering iron-carbon alloys. For the production of these new materials, it is essential that a sufficiently large amount of nitrogen above the solubility limit under normal pressure is introduced into the molten steel and that nitrogen loss is prevented during solidification. As the solubility of nitrogen is proportional to the square root of its partial pressure (Sievert's law), it is possible to introduce large amounts of nitrogen into the melt and allow it to solidify under higher pressure.<sup>14,15</sup> This has been verified by the electroslag remelting process at an operating pressure of 42 bar. Due to the extremely short dwell time of the metal droplets in the liquid phase during remelting, the nitrogen pick-up via the gas phase is insufficient. The nitrogen must, therefore, be supplied continuously during remelting in the form of solid nitrogen-bearing additives. The high pressure in the system serves exclusively to retain the nitrogen introduced into the melt. The pressure level depends on the composition of the alloy and on the desired nitrogen content of the remelted ingot.

#### *Electroslag remelting under inert gas atmosphere (IESR)*

As a consequence of ALD's development work in PESR processing,<sup>14,16</sup> ALD nowadays recommends that the ESR process should be conducted under a fully enclosed inert gas atmosphere at atmospheric pressure. This is a great step forward in freeing the ESR process from hydrogen pick-up problem and the influence of seasonal atmospheric changes. In addition it allows remelting under oxygen-free inert gas. The following results have been obtained:

- Oxidation of electrode and slag is completely avoided;
- Oxidizing loss of elements such as Ti, Zr, Al and Si is almost completely avoided. This is especially important when remelting high Al- and Ti-containing alloys, such as super alloys with very narrow analytical ranges;

- Better cleanliness in the ingot is achieved;
- When using argon as the inert gas, pick-up of nitrogen and hydrogen is avoided; (when using nitrogen as the inert gas, some pick-up of nitrogen is possible). Due to the absence of oxygen in the furnace atmosphere, desulphurization via the gas phase is no longer optimal. However, sulphur is today taken care of by ladle metallurgy in the making of steel electrodes.

Two furnace concepts are available: one with a protective hood system of relative tightness and the other with a fully vacuum-tight protective hood system that allows the complete exchange of air against an inert gas atmosphere prior to starting the remelting process.

## 29.4 Modelling Issues of Stainless Steel Converter Processes

For quantitative description and understanding the refining of stainless steel in different converters, mathematical models are extremely useful because they simulate the actual process. They are able to unravel the influence of the different process parameters, and a variety of models for converting processes have been developed.<sup>10-12</sup> During a converting process, different homogeneous and heterogeneous reactions can take place, for example, decarburization and oxidation of the molten metal, reduction of the slag, post combustion in the gas phase, dissolution of additions in the metal phase, and formation of complex slag compounds. Converter processes are also strongly affected by process parameters, such as temperature, composition, converter geometry, and gas flow rate. Therefore, converting processes are complex processes.<sup>13-14</sup> Models based on transport phenomena, CFD and chemical kinetics are important tools for characterization of such processes to obtain greater insight of dynamic behaviour of the reactor.

### 29.4.1 Rate equations describing evolution of concentration

The evolution of the concentration of a component in a converter processes can be expressed in a generic form:<sup>17,18</sup>

$$\frac{\partial c_i}{\partial t} = \frac{N_i A}{V} \quad (29.1)$$

The expression for total molar flux can be given as:

$$N_i = k_i c(x_i^o - x_i^\infty) + x_i \sum_{j=1}^m N_j \quad (29.2)$$

The equation for total molar flux for components in the metal and slag phases:

$$N_i = k_i^{met..slag} c(x_i^{eq} - x_i^b) \quad (29.3)$$

The equation for total molar flux for components in the gas phase is:

$$N_i = k_i^{gas} c(x_i^{eq} - x_i^b) + x_i^{eq} \sum_{j=1}^m N_j \quad (29.4)$$

where,  $C_i$  is the molar concentration of component  $i$ ,  $t$  is time,  $N_i$  is total molar flux of component  $i$ ,  $A$  is area of interface,  $V$  is volume of phase,  $k_i$  is the mass transfer coefficient of component  $i$ ,  $c$  is molar density,  $x_i$  is mole fraction of component  $i$ ,  $x_i$  is interface concentration,  $x_i^\infty$  is steady state concentration,  $x_i^{eq}$  is equilibrium concentration,  $x_i^b$  is bulk concentration,  $k_i^{met.slag}$  is the mass transfer coefficient from metal to slag phase and  $k_i^{gas}$  is the mass transfer coefficient of the gas phase.

## 29.2 Computational Fluid Dynamic (CFD) Modelling of Converter Process

Steady and unsteady CFD modelling can be applied to simulate fluid flow species transfer, combustion and heat transfer phenomena in the stainless steel converter such as AOD and VOD. Appropriate assumptions are imperative to construct the CFD models to simulate the transport phenomena issues. Turbulent momentum transferring, energy transferring including radiation and species transferring with volume reaction can be modelled in a coupled manner.

The governing CFD conservation equations to simulate the stainless steel converter transport processes are:

*Continuity equation*

$$\frac{\partial \rho}{\partial t} + \nabla \cdot (\rho \mathbf{u}) = 0 \quad (29.5)$$

*Momentum conservation equation*

$$\frac{\partial \rho \mathbf{u}}{\partial t} + \nabla \cdot (\rho \mathbf{u} \mathbf{u}) = -\nabla p + \nabla \cdot \mathbf{\tau} + \mathbf{F}_s \quad (29.6)$$

*Energy conservation equation*

$$\frac{\partial}{\partial t}(\rho h) + \nabla \cdot (\rho \mathbf{u} h) = \nabla \cdot \left( k_{eff} \nabla T - \sum_j h_j \bar{j}_j \right) + S_h \quad (29.7)$$

*Species conservation equation*

$$\frac{\partial}{\partial t}(\rho Y_i) + \nabla \cdot (\rho \mathbf{u} Y_i) = -\nabla \cdot \bar{J}_i + R_i \quad (29.8)$$

where,  $\rho$  is density,  $\mathbf{u}$  is velocity,  $t$  is time,  $T$  is temperature,  $p$  is pressure,  $\mu$  dynamic viscosity,  $\mathbf{F}_s$  is momentum source term,  $k_{eff}$  is effective conductivity,  $S_h$  is heat source related to chemical reaction and radiation and  $h$  is sensible enthalpy, defined as  $h = \sum_j Y_j h_j$ ,  $Y_i$  is

the mass fraction of species  $j$ ,  $h_j = \int_{T_{ref}}^T C_p dT$ . Some of the typical CFD modelling results are shown here.<sup>19</sup> Figure 29.10 shows the gas velocity vector field near the AOD mouth, which suggests that the most of hot gas from converter will flow directly to the ventilation hood. For this stable case no entrapped air flow into the converter is observed.

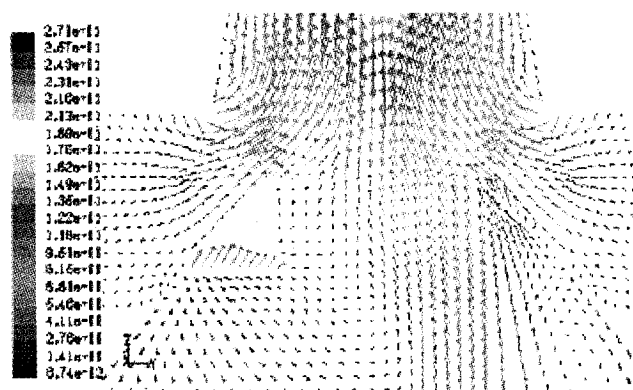


Fig. 29.10 Velocity vector of mixture gas on the symmetric plane near the mouth of the AOD.<sup>19</sup>

A typical CFD simulation of nitrogen contour on the mouth plane of AOD converter is shown in Fig. 29.11. The figure shows that the nitrogen content is high near the edge of the AOD mouth and low at its centre. This indicates that the most hot gas inside converter flow directly from the centre part of AOD and pushes away the intruded cold air. Cold air from outside only slips along the sides of the AOD mouth into the converter.

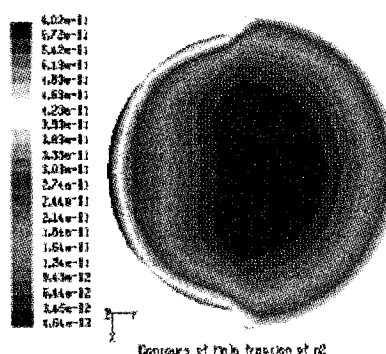


Fig. 29.11 Nitrogen contours on the mouth plane of the AOD.<sup>19</sup>

A typical computational map of the nitrogen content at the outlet of the exhaust gas hood is shown in Fig. 29.12. The results indicate that the volume fraction of nitrogen at the end of the hood ranges from 73.5% to 78%. The nitrogen does not get distributed evenly on the outlet plane. Figure 29.13 shows a typical simulated carbon dioxide distribution on the

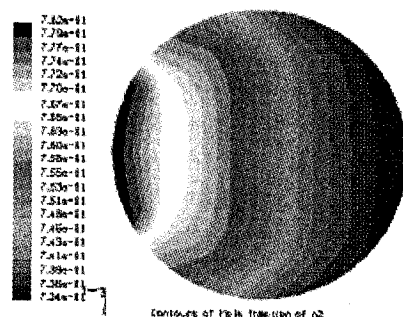


Fig. 29.12 Nitrogen contours at the outlet of the hood.<sup>19</sup>

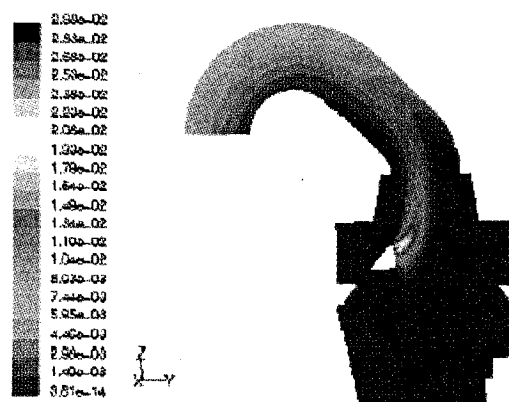


Fig. 29.13 Carbon dioxide distribution on the symmetric plane of AOD.<sup>19</sup>

symmetric plane of AOD. It further suggests that carbon dioxide is produced at the areas a little above the left part of AOD mouth, which is an indication of good level of mixing of carbon monoxide with the air.

Figure 29.14 is a typical depiction of nitrogen content along the centre line of the stainless steel converter at different time of one pressure oscillation period. The results further suggest that the nitrogen fraction is always far below 2% within the height of 1.5 meters from the bath surface under different hood suction ability conditions.

## 29.5 Future Perspectives

Selection of the most practical and economic process route for stainless steel making depends on many factors including consideration of availability and cost of raw materials availability and costs, productivity requirements, product mix, existing shop equipment and logistics, and capital and operating costs. Other important factors may include general business conditions, financial status of the steel producer and consolidation of steel making facilities, plant closures, competency of available manpower, and social and political factors. The fact



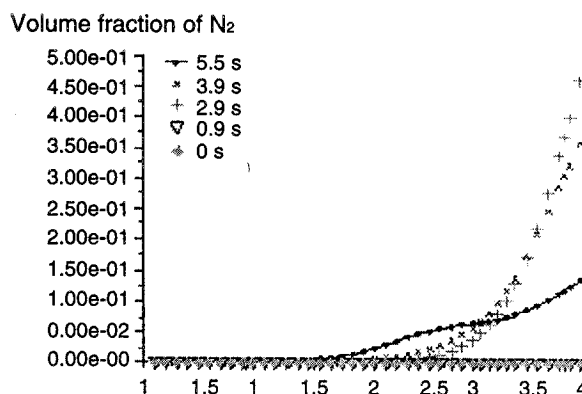


Fig. 29.14 Nitrogen fraction along the height of AOD.<sup>19</sup>

that many of the above factors may change over time suggests that the most flexible process route must be chosen. The percentages of stainless made by converter/VOD process routes will increase at the expense of converter-only and vacuum-only processes in consonance with global trends. Hot metal supply from sources other than the arc furnace will become more common, particularly in developing countries such as China and India.

Process optimization, automation and control will continue to grow at a rapid pace in the existing and new secondary steel making installations. Computer based process models will be implemented in the plants to predict end point carbon and temperature control more accurately; the trend toward shorter vessel tap-to-tap times will continue and there will be increased utilization of post converter treatment and optimization of sequence casting. The use of on line slag analyses will be expanded to facilitate these improvements. The continued evolution and development of top lance designs will result in optimization of post combustion in both hard and soft blow practices. There will be further application of fuels and mixed gases in top lances. The use of non-cryogenic on-site gas production facilities (pressure swing absorption and membrane) to supply oxygen and nitrogen may become more common. Eventually, argon recycling in combination with a closed hood, off-gas, and a heat recovery system will be applied in future installations. The application of irregular shaped tuyeres, stainless dephosphorization, powder injection and slag splashing in converters will be further improved to attain high process efficiency and productivity.

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